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Abstract. The removal of methyl orange (MO) dye using porous chitosan (CS) gel beads was investigated in a batch mode. The newly formed porous CS gel beads were synthesized by using a solidification bath containing mixture of NaOH-Na_2CO_3 at ratio of 1:1. Orthogonal array of L_9 (3^3) was used to generate nine sets of experiments based on three controlling factors: initial dye concentration (30 ppm, 50 ppm, 90 ppm), adsorbent dosage (0.35 g, 0.5 g, 1 g) and pH of MO (pH 3, 7, 11).The highest mean of Signal to Noise (S/N) ratio was chosen to obtain maximum adsorption capability of newly formed porous CS gel beads. The optimum operating conditions to maximise the removal percentage ($R\%$) were identified as 1 g of adsorbent dosage, 30 mg/L of initial MO concentration at pH 3, whereas maximum equilibrium uptake capacity (q_e) of 10.41 mg/g was achieved by dosing 0.35 g of adsorbent dosage into 90 mg/L of initial MO concentration at pH 3. ANOVA studies were also carried out to study the contribution percentage of each designed parameter. The results indicated that the initial concentration and pH of MO dye solution have the biggest contribution to $R\%$ and q_e, respectively.

1. Introduction

The vast amount of dye wastewater generated from textile industry has become one of the worldwide problems. The dye effluent has then been absorbed by flora and fauna and caused secondary pollution on ecosystem [1]. To mitigate the water pollution , Malaysia established Water Services Industry Act 2006 to regulate water supply and sewarage services of industry. However, some local textile manufacturers still experience high COD concentration in the final effluent exceeding the standard discharge limit due to the presence of unbiodegradable dye molecules [2]. Thus, extensive research on alternative treatments is required to sustain this industry.

Dye wastewater can be generally treated by chemical, biological and physical methods [3]. Nevertheless, adsorption is preferable in wastewater applications due to its simple operation, high removal efficiency, and low cost [4]. In recent years, chitosan (CS) has been widely studied as an adsorbent to prove its effective adsorption capacity [5]. CS is a natural biopolymer derived from the polysaccharide known as chitin through hydrolysis process [6]. CS is also one of the low cost absorbents used to remove pollutants from effluent [7].Various studies involved the use of CS in

wastewater treatment were carried out and showed that CS-based adsorbents are not only effective in anionic dye removal as well as in removing heavy metals [8]. Various manipulated variables such as pH, initial dye concentration, temperature, and adsorbent dosage are generally selected to study their responses to the adsorption efficiency [9]. From economic and environmental aspects, the optimum conditions should be determined to maximize the removal percentage (*R%*) and uptake capacity (q_e) simultaneously [10]. The least amount of adsorbent dosage with the highest *R%* is favorable to achieve economic feasibility. In the meantime, low q_e should be avoided to reduce the amount of waste products generated after dye removal. Notably, the most dominant physio-chemical factor of adsorbent that can affect the performance of decolourization is its surface area. An adsorbent with higher porosity is always characterized with higher surface area which in turn increases its adsorption capacity [3]. The synthesis of adsorbents using porogenic solvents has been reported to produce porous solid [11]. Porogenic solvents were previously investigated such as coffee residue, sodium hydroxide, bentonite and sodium carbonate [12].

In present study, a one-step approach of NaOH-based solidification bath supplemented with a pore-forming agent, sodium carbonate (Na_2CO_3) was developed herein to increase the effective surface area and porosity of CS gel beads. This approach was aspired by a studied conduct by Wahba [11], as he successfully synthesized porous CS gel beads by mixing Na_2CO_3 and ionotropic gelation solution, tripolyphosphate (TPP) to increase the amount of active sites for enzymes immobilization. On top of that, the coupling method of phase inversion process with porogen in the synthesis of porous CS beads has never been investigated for water applications to the best of our knowledge. Taguchi method, L9 (3^3) orthogonal array, with three factors at three levels and nine rows, was selected to optimize the adsorption response (*R*% and q_e) and determine the optimum operating conditions of the MO adsorption using porous CS gel beads. Signal-to-Noise (S/N) ratio and analysis of variance (ANOVA) were also carried out to study the significance of the parameters on the dye removal of Methyl Orange (MO). The major aim of this research was to determine the adsorption capability of porous CS gel beads for the removal of MO dye by using Minitab 18.

2. Materials and Methods

2.1. Synthesis of porous CS gel beads

A mixture of chitosan-acetic acid (CS-AA) was initially prepared by dissolving 6 g of CS powders in 194 g of AA (3 wt%) to make up 3 wt% of CS solution. The mixture was then stirred at room temperature for 3 h until homogenous mixture was obtained. A volume ratio of NaOH (1 M) to Na_2CO_3 (0.6 M) solution at 1:1 was used to form the porous CS gel beads in 200 mL of beaker by dripping CS solution dropwise through a 1-mL capacity of disposal plastic syringe with a 22G needle tip by using a syringe pump (NE-1000, Netherlands) operated at 0.5 ml/min. To remove the alkaline residue on porous CS gel beads, the beads were then rinsed thoroughly with distilled water until neutral pH. After that, the porous CS gel beads were dried at 60°C for 24 h.

2.2. Batch adsorption studies

Three manipulating variables such as pH of MO dye solution, initial MO dye concentration and dosage of adsorbents were studied to determine the adsorption performance of porous CS gel beads. Batch adsorption experiments were carried out by following the stipulated conditions generated from Taguchi approach (see table 1) with utilizing a fixed volume (50 mL) of MO dye solutions, stirred at 200 rpm in an incubator shaker at 21°C, unless stated otherwise. At predetermined time intervals, a fixed amount of sample was withdrawn from the mixture and the concentration of treated MO dye solution was determined using spectrophotometric. The *R*% and q_e [42] of adsorbent were determined by using equation (1) and (2):

$$R\% = \frac{C_o - C_t}{C_o} x\ 100\% \quad (1)$$

$$q_e = \frac{(C_o - C_t)V}{m} \quad (2)$$

where R% is removal percentage of dye (%), q_e is uptake capacity of porous CS gel beads at equilibrium condition (mg/g), C_o is initial MO concentration (ppm), C_t is initial MO concentration at t time (ppm), V is volume of MO dye solution (L) and m is mass of porous CS gel beads (g).

2.3. Optimization: Taguchi design and methodology

Three manipulated variables along with 3 levels were tabulated in table 1. L9 (3^3) orthogonal array based on Taguchi method was used to determine the optimum operating condition with minimized number of experiments. Thus, nine different sets of adsorption experiments were then carried out (Table 1). Subsequently, 50 mL of MO dye solution with different dosage of adsorbent, pH and initial MO dye solution were poured into 200 mL of conical flask and swirled by using an incubator shaker (IKA KS 4000 i control shakers, Malaysia) at 200 rpm and ambient temperature. 0.05 M NaOH and 0.5M HCl were used to adjust the pH of MO dye solutions. Signal to Noise (S/N) ratio was computed by using Minitab 18 package to determine the degree of deviation between actual and idea data. S/N ratio of "larger is better" category was selected to find the optimum condition where porous CS gel beads could perform effectively by optimizing the R% and q_e [10].

Table 1. L9 (3^3) orthogonal array with three controlling factors at 3 levels and set order for each replication.

Set	Controlling Factors		
	pH	**Initial MO Concentrations C_{0MO} (ppm)**	**Adsorbent Dosage m (g)**
1	3	30	0.35
2	3	50	1
3	3	90	0.5
4	7	30	0.5
5	7	50	0.35
6	7	90	1
7	11	30	1
8	11	50	0.5
9	11	90	0.35

3. Results and Discussions

Smooth surface is observed in pure CS gel beads in figure 1(a). After treatment with pore forming agent, Na_2CO_3, the morphological changes of CS gel beads were clearly illustrated in figure 1(b). Treated CS gel beads were characterised to have rough and porous surface with various sizes of cavities. Figure 1(c) reveals that porous CS beads possessed higher R% (73%) in comparison with pure CS beads (67%) due to the presence of active sites on the treated porous CS beads' surface.

As illustrated in figure 2, the results revealed the amount of MO dye adsorbed increased with initial MO concentration at constant adsorbent dosage. This is mainly because the higher MO concentration increased the driving force of concentration gradient [13]. Besides, maximum adsorption capability was observed at pH 3 of dye solution due to the electrostatic attraction between MO dye molecules and CS gel beads. More protons existed at lower pH which allowed the protonation of amino groups in CS resulted in increase in the electrostatic attraction of dye molecules onto active sites of CS beads [4].

S/N ratio of each set was computed by using "larger is better" type of S/N ratio plot to find the best condition where maximum of R% and q_e were obtained. According to figure 2, the average R% was between 30.09% and 98.15% whereas the average q_e value varied from 1.22 mg/g to 9.14 mg/g. The highest S/N ratio was selected as the optimum condition where the highest R% achieved was

determined as 1 g of adsorbent dosage, 30 mg/L of initial MO concentration at pH 3. In contrast, the optimum condition for maximising q_e was identified as 0.35 g of adsorbent dosage, 90 mg/L of initial MO concentration at pH 3.

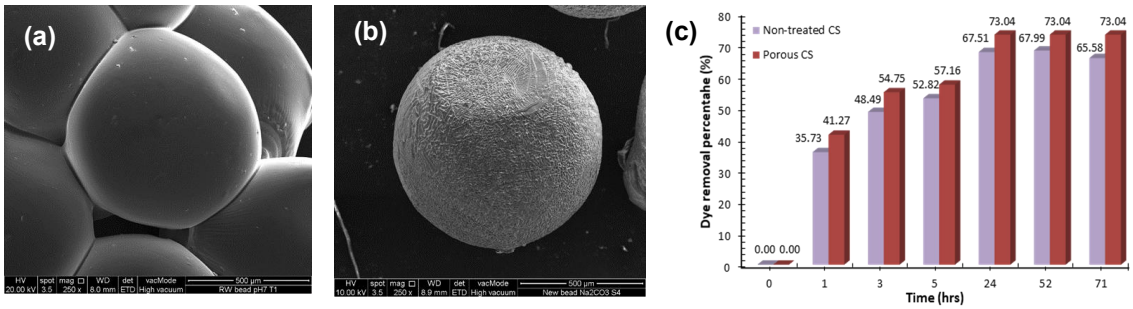

Figure 1. FESEM of (a) Non-treated pure CS beads and (b) Porous CS beads at magnification of 250x (c) R% of both types of CS.

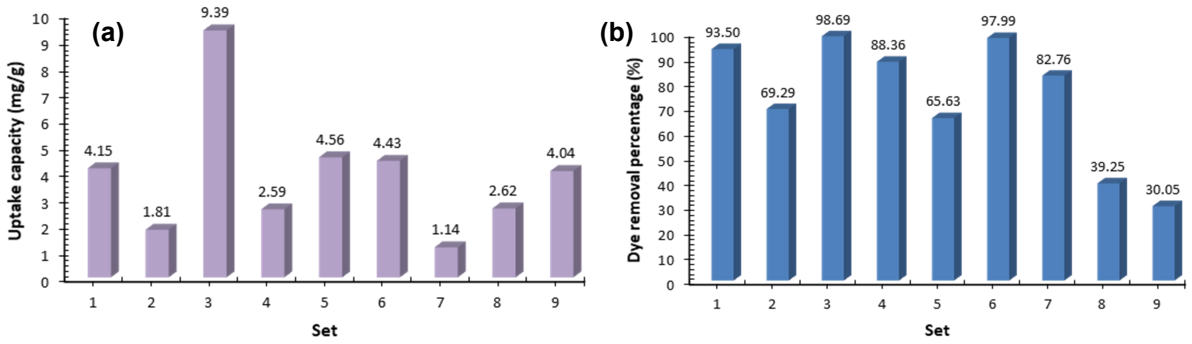

Figure 2. Effect of porous CS gel beads on (a) uptake capacity and (b) *R%*.

The significance of each possible combination was determined using ANOVA computed from Minitab 18. According to the contribution percentage tabulated in table 2, the pH of MO dye solution had the highest contribution percentage in affecting the R%. However, the initial concentration of MO dye solution predominantly regulated the q_e of adsorbents.

Table 2. Contribution percentage of designed factor for both adsorption responses.

Designed factor	Contribution percentage (%)	
	R%	q_e
Dosage	-	16.62
Concentration	1.62	40.02
pH	38.43	19.21
Dosage*pH	-	13.97
Concentration*Concentration	24.75	-
pH*pH	9.87	-
Concentration*pH	16.7	7.33
Concentration*pH*pH	8.04	-
Error	0.59	2.86

4. Conclusion

The newly formed porous CS gel beads used to remove MO dye molecules from aqueous solution were synthesized via neutralisation of acetate functional groups with the mixture of NaOH-Na_2CO_3. FESEM analysis showed that the adding of Na_2CO_3 induced pore formation on the surface of CS gel beads and hence enhanced the actives sites of CS adsorbents. The optimum conditions for *R*% were obtained under such conditions: 1 g of CS dosage, 30 mg/L of initial MO concentration at pH 3. Meanwhile, 0.35 g of CS required to dose into 90 mg/L of initial MO concentration at pH 3 was required to achieve the highest q_e. Both results revealed the electrostatic adsorption was favoured at acidic media. Based on ANOVA analysis, the pH of MO dye solution contributed the highest percentage (38.43%) in affecting *R*% whereas q_e was mainly affected by initial MO concentration with the percentage of 40.02%.

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